KINETICS OF BROWN COAL GASIFICATION

R. Hegermann, K.J. Hüttinger
Institute of Chemical Technology
University of Karlsruhe, Kaiserstr. 12
Federal Republic of Germany

ABSTRACT

The kinetics of brown coal gasification in CO_2 and steam at various pressures and temperatures were studied by using a fluidized bed reactor. Gasification kinetics are nearly completely controlled by mineral matter, preferentially calcium. At all conditions the gasification behaviour may be described by the following semi-empirical model.

$$r = \frac{2 \cdot Y_{(max)} \cdot X}{X_{(max)}} - \frac{Y_{(max)} \cdot X^2}{X_{(max)}^2} + (a+bX)^{1/2} \cdot (1-X)^{2/3}$$

This equation is based on a particle model ($(1-X)^{2/3}$) which additionally considers a probable catalyst activation or deactivation with progressive gasification ($(a+bX)^{1/2}$) and finally the initially fast coal gasification ($2 \cdot Y_{(max)} \cdot X/X_{(max)} - Y_{(max)} \cdot X^2/X_{(max)}^2$).

INTRODUCTION

Brown coal seems to be an attractive raw material for gasification, because it is believed to be very reactive. The development of gasification processes requires fundamental knowledges about the reactivity in various atmospheres and in view of modern gasification technologies especially at high pressure. Gasification studies were performed at constant temperatures and pressures using a fluidized bed of alumina particles, into which the brown coal was charged. The gasification rates in various atmospheres were measured by on line gas analysis using IR-analyzers and a gaschromatograph. The changes of internal surface area with progressive gasification were determined by carbon dioxide and nitrogen adsorption. For analysis of the gasification mechanism studies with demineralized coal were performed.

EXPERIMENTAL

Three types of Rheinische Braunkohle were used in these studies (1), but only the results of a typical coal will be presented. The analytical data of this coal are given in Table 1. The special property of the coal is that the content of mineral matter merely varies with particle size. The majority of the studies were performed with a particle size fraction ranging from 2 to 3 mm. All samples were carefully dried. For demineralization the coal was treated with conc. HCl/HF (1:1). For further studies calcium was introduced into the demineralized coal by ion exchange using $CaCO_3$.

The experimental equipment used for the gasification studies and the special analytical procedure for an accurate measurement of the gas formation peaks resulting in a batchwise experiment are reported elsewhere (2). Coal samples of 100 to 150 mg were used. Each experiment was done twice.

RESULTS

Gasification kinetics of dry coal

In all experiments the formation rates of all product gases were measured. In the following Figures the carbon conversion to gases, termed as gas yield, are presented as function of the reaction time (series a). The rates of carbon conversion to gases, termed as gasification rate, as function of the normalized gas yield are additionally presented (series b). The latter Figures give further informations about the mode of gasification kinetics (kinetic model). The yields and gasification rates are related on the initial amount of carbon of the coal.
Figs.1 and 2 show the results of gasification with pure CO_2 at four different pressures and at temperatures of 800°C (Fig.1) and 900°C (Fig.2). At both temperatures the gas yields are nearly independent on pressure and amount to roughly 80 %. This means that approximately 20 % of volatiles are formed. The gasification is completed after 1000 to 2000 s (800°C) or 500 to 1000 s (900°C). The pressure influence is anomalous or at least surprising. The rates increase with pressure only up to 0.5 MPa (800°C) or 1.0 MPa (900°C). Fig.3 shows analogous results for gasification with steam by using an argon/steam mixture (1:1) at total pressures of 1.0 and 2.5 MPa. Especially at 800°C the gasification rate is decisively higher than with CO_2, although the steam partial pressure is only 50 % of the CO_2 pressure at each total pressure. The gas yields are similar to those obtained in gasification with CO_2. The anomalous pressure influence can directly be observed at 800°C, at 900°C the rate at 2.5 MPa total pressure (corresponding to pH_2O= 1.25 MPa) is slightly higher than at 1.0 MPa (pH_2O= 0.5 MPa), which also corresponds to the results of CO gasification. It may be expected that the pressure influence becomes negative at 900°C, if the total or partial pressure of pH_2O is further increased.
The reasons for the negative pressure effect at high partial pressure may be (a) a different degassing behaviour at high pressures or (b) a special property of a catalyzed gasification. The explanation will be given in the following chapters.
Fig.4 shows the influence of hydrogen on the steam gasification at 1.0 MPa and 800°C using an $Ar/H_2O/H_2$ mixture (2.5:5:2.5). Hydrogen strongly inhibits the gasification reaction. After 3000 s the gasification rate is nearly zero, although 34 % of the carbon are not yet gasified. Inhibition of non-catalyzed steam gasification is known by numerous studies, but a complete inhibition has not yet been reported.

Changes of internal surface area

The Figures of series b reveal that the gasification of the brown coal does not follow one of the known models (volume, particle,

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pore).This still holds, if it is assumed, that the steep increase of the gasification rate at low carbon conversions (Figs. of series b) is a consequence not of the reaction but of the on-line gas analysis, which may be possible. Nevertheless, the changes of the BET surface area with progressive gasification have been determined for some cases.
Fig. 5 shows the BET surface area in dependence on the normalized gas yield for gasifications at 800°C and at pressures of 1.0 and 2.5 MPa. Although it is well known that only the CO_2 adsorption gives reasonable results, the N_2 adsorption was studied for demonstrating the differences between CO_2 and N_2 adsorption kinetics. At both gasification pressures the BET surface area passes through a maximum. A comparison with the Figs. 1b and 2b yields no conformity of the curves. In any case, it may be concluded that the maxima of the BET surface area occur at higher gas yields than the maxima of the gasification rates. This means that the BET surface area obviously has a minor importance for the gasification kinetics.
Fig. 6 shows similar results for the gasification with steam at 1.0 MPa and 800°C using an argon/steam mixture (1:1). The conclusions are the same as drawn for the gasification with CO_2.

Gasification kinetics of 'demineralized' coal

Studies with demineralized coal were performed in order to clarify a possible catalytic effect of mineral matter. By demineralization with HCl/HF the mineral matter could completely be removed from the coal. Gasification studies with such coals were performed at 1.0 MPa and at temperatures of 800°C and 900°C using CO_2 (Figs. 7 and 8) and steam (Fig. 9). The Figs. 7a and b show that the gasification rate of the demineralized coal approaches to zero after 10 % of the carbon are gasified. At 900°C (Figs. 8a and b) the gasification rate is zero after about 2 hours gasification. At that time only 70 % of the carbon are gasified. On the contrary, gasification of the original, non-demineralized coal is already completed after 500 s. These comparison underlines the strong catalytic effect of the minerals. Calcium was believed to be the main active component, because the content of the alkali metals of the coal is negligibly small. By ion exchange 39 % calcium of the original calcium content of the coal could be introduced into the demineralized coal. This doped coal confirms the strong catalytic effect of the calcium, especially at 900°C (Figs. 8a and b).
The steam gasification with demineralized coal yields similar results as found in CO_2 gasification (Figs. 9a and b). Due to the higher reactivity of steam, the effect of demineralization is not as strong as compared to CO_2 gasification. Nevertheless, at 800°C the gasification rate approaches to zero before all carbon is gasified (Fig. 9b).

DISCUSSION

The gasification kinetics of a Rheinische Braunkohle with CO_2 and steam was studied at pressures up to 2.5 MPa and at temperatures of 800°C and 900°C. The gasification rates of steam gasification are higher, but the increase of the gasification rate with partial pressure is limited for both gases. Above 0.5 MPa (800°C) and above

1.0 MPa (900°C) the rates decrease with further increasing pressure.
This pressure effect on the gasification rate was unexpected. Gasi-
fication studies with demineralized coal show that brown coal or
brown coal coke without cations are extremely unreactive. Further
studies with a demineralized coal, but doped with calcium (0.5 wt%)
envisualized the strong catalytic effect of this element. Therefore,
it may be concluded that the high reactivity of the brown coal main-
ly or exclusively results from the minerals or more precisely from
the calcium, because the content of alkali metals is negligibly
small.
The gasification kinetics with progressive consumption of coal or
coke may be described neither by a volume, pore or particle model
(2). This conclusion clearly follows from the plots of the gasifi-
cation rates versus carbon conversion (normalized carbon yields,
Figs. 1b and 2b). It is underlined by the plots of specific surface
area versus carbon conversion (Figs. 5 and 6). In fact, the gasifi-
cation is determined by three processes: (1) Fast gasification of
the coal at the beginning, i.e. at low carbon conversions. In this
stage the gasification rates may be extremely high. (2) Control of
the gasification in the coke gasification stage by catalysis. In
this stage the specific surface area should be of minor importance.
(3) Increase of the catalyst concentration with progressive gasifi-
cation. This point may be important, because the initial concentra-
tion of calcium is small (1.3 wt%). Instead of a catalyst concentra-
tion increase a progressive activation of the catalyst may be opera-
tive (steam gasification). The probability of this interpretation is
supported by the experimentally observed decreasing activity in the
case of the CO_2 gasification. In view of the latter interpretation
of the gasification kinetics it is unprobable that the improved
accessibility of the internal surface with progressive gasification
plays a major role.

In consideration of these processes the following semi-empirical mo-
del was derived:

$$r = \underbrace{\frac{2\,Y_{(max)}\,X}{X_{(max)}} - \frac{Y_{(max)}\,X^2}{X_{(max)}^2}}_{F_3} + \underbrace{(a+bX)^{1/2}}_{F_2}\underbrace{(1-X)^{2/3}}_{F_1}$$

F1 = particle model; F2 = catalyst activation or deactivation with
progressive gasification; F3 = fast coal gasification; $X_{(max)}$ =
carbon conversion at highest gasification rate; $Y_{(max)}$ = highest
gasification rate.

With this model the gasification kinetics of the coal may be des-
cribed at all conditions. Examples are given in Figs. 10 and 11.

The differences between the experimental points and the calculated
curve at the very low carbon conversions are mainly ascribed to the
measurement of the gas formation rates.

REFERENCES

(1) Hegermann, R., Ph.D thesis, University of Karlsruhe, in
    preparation
(2) Hüttinger, K.J., in: New Trends in Coal Science (Yuda Yürüm,Ed.)
    (1987), 433 and 453, NATO ASI Series

Table 1 - Elemental analysis and composition of a typical Rheinische
          Braunkohle (mf); ash content (wt %): 6.7

Elemental analysis (wt %)		ash composition (wt %)	
		Na_2O	0.3
C	60.1	K_2O	0.2
H	4.9	CaO	27.5
N	1.0	MgO	8.6
S	0.9	Fe_2O_3	11.7
O (diff.)	33.1	Al_2O_3 SiO_2	40.0
		SO_3	11.6

Fig 1a

Fig 1b

CO_2 gasification at 800 °C; gasification rates are generally
given as $10^5 \cdot mol_{C_{gas}} \cdot mol_{C_o}^{-1} \cdot s^{-1}$

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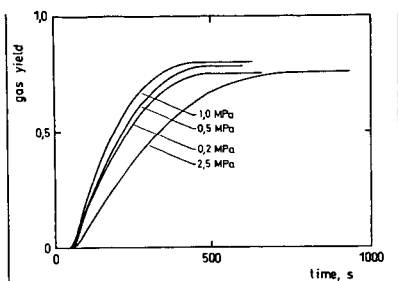
Fig 2a
CO_2 gasification at 900 °C
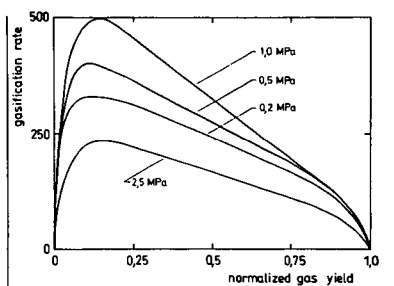
Fig 2b
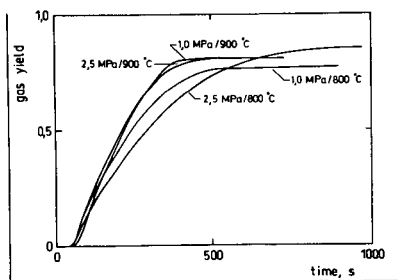
Fig 3a
Steam gasification at 800 °C and 900 °C
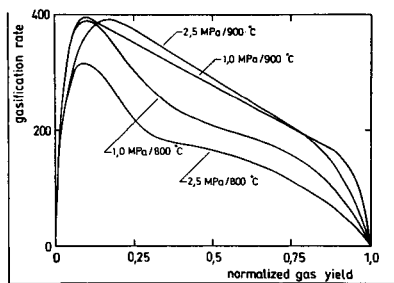
Fig 3b
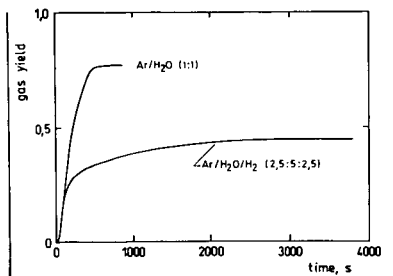
Fig 4a
Steam gasification at 1.0 MPa and 800 °C, influence of hydrogen

Fig 4b

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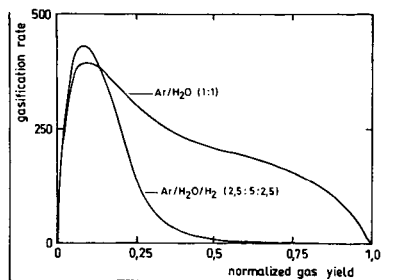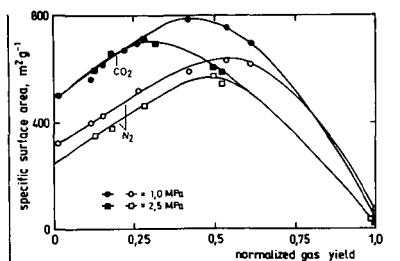
Fig 5

Change of specific surface area during CO_2 gasification at 800 °C
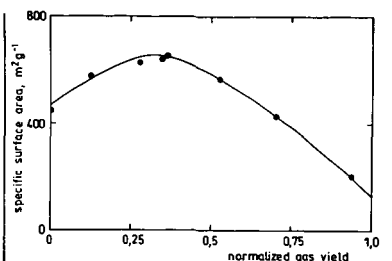
Fig 6

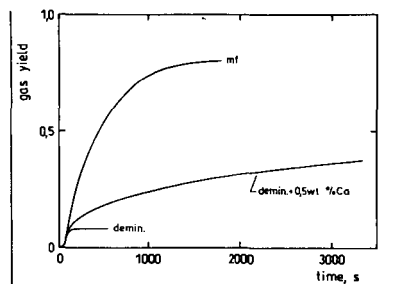Change of specific surface area during steam gasification at 800 °C

Fig 7a

Fig 7b

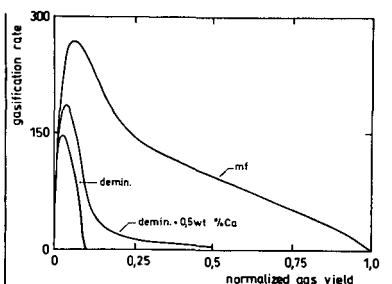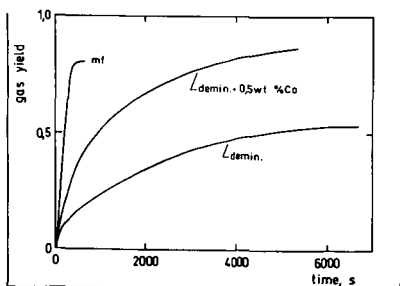CO_2 gasification of 'demineralized' coal at 1.0 MPa and 800 °C

Fig 8a

Fig 8b

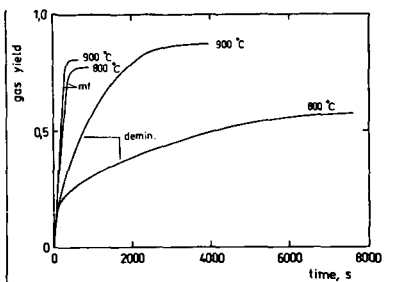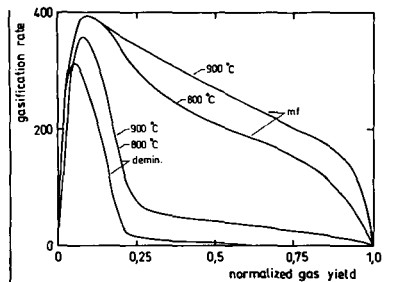CO_2 gasification of 'demineralized' coal at 1.0 MPa and 900 °C
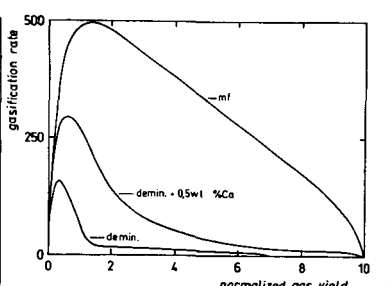
Fig 9a

Fig 9b

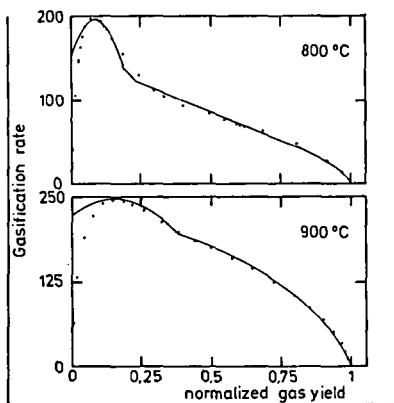Steam gasification of 'demineralized' coal at 1.0 MPa

Fig 10

Exemplary check of the semi-
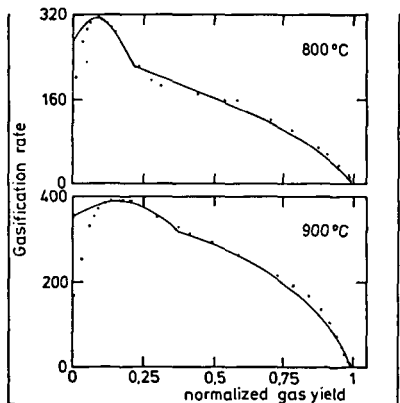empirical equation for CO_2
gasification at 2.5 MPa

Fig 11

Exemplary check of the semi-
empirical equation for steam
gasification at 2.5 MPa

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